Measurements and Correlation of High-Pressure VLE of Binary CO_2-Alcohol Systems (Methanol, Ethanol, 2-Methoxyethanol and 2-Ethoxyethanol)

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Abstract

High-pressure vapor-liquid equilibrium data were measured for binary CO_2-alcohol systems (e.g., methanol, ethanol, 2-methoxyethanol, and 2-ethoxyethanol) at various isotherms (313.15 ~ 345.15K). The quantitative VLE data and mixture critical conditions were measured using a designed new circulation VLE system. The measure data were correlated by the classical Peng-Robinson and the MF-NLF-HB(multi-fluid nonrandom lattice fluid hydrogen-bonding) equation of state. The MF-NLF-HB model was formulated previously by the present authors based on the proton donor-acceptor principle to the hydrogen-bonding interaction in CO_2-alcohol systems. For the measured and calculated data of CO_2-alcohol systems, relative accuracy of the data were discussed.

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1. Introduction

Thermodynamic knowledge of high-pressure phase equilibrium data of fluid mixtures as well as pure fluids plays essential role on the efficient basic design of various separation processes in such fields as natural gas, oil and numerous fine chemical industries. As a result, attention has been placed on the thermodynamic understanding of fluid systems. Also, during the last two decades, efforts have been focused on the quantitative understanding of phase equilibrium behaviors of fluids near the critical region of mixtures as well as pure fluids due to the emerging technology of supercritical fluids [1,2]. The information of high-pressure behavior of fluids at supercritical state has been valuably used to design new separation processes in various fields such as food, pharmaceutical and fine chemical industries [3]. Especially, the high-pressure phase equilibrium information of mixtures composed of CO_2 and alcohols have been actively studied for various utilities. For example, the phase equilibrium behaviors of low molecular weight alcohols such as methanol and ethanol in CO_2 is essential to the effective searching of cosolvent to CO_2-based supercritical solvents [4]. Also the phase equilibrium information of high molecular weight alcohols such as 2-ethoxyethanol with CO_2 is valuably used to processes in food and cosmetic industries.

In addition, efforts have long been placed on the devising various experimental apparatus for the measurement of high-pressure phase-equilibrium data of vapor and liquid mixtures. For example, techniques of *in situ* installation of chromatograph and spectroscopic analytic tools and sampling devices are widely used to date [5]. Among them, a new circulation-type experimental apparatus was designed and it was used to measure the VLE data of CO_2-alcohol systems in the present study. A detailed

description of the apparatus was made in the next section.

To test the reliability of the newly designed experimental apparatus, two of illustrative binary systems such as CO_2-methanol and CO_2-ethanol was chosen and necessary VLE data were measured. After confirmation, the apparatus was used to measure new VLE data for CO_2-2-methoxyethanol and CO_2-2-ethoxyethanol systems.

Due to the existence of hydrogen-bonding, it was frequently difficult to correlate quantitatively the VLE data of CO_2-alcohol systems. Thus in the present study, effort was made to model the measure VLE data by a traditional Peng-Robinson equation of state (EOS) [6] and by a new EOS named as the MF-NLF-HB. The MF-NLF-HB EOS was recently proposed by the present authors elsewhere based on the nonrandom lattice-fluid theory combined with the effect of hydrogen bonding [7,8]. Finally the advantage and shortcoming of the MF-NLF-HB for the correlation of CO_2-alcohol systems was discussed.

2. Experimental Section

2-1. Chemicals

CO_2 (>99.9% purity) was purchased from Seoul Special Gas Co. (Seoul, Korea) and used without further purification. Methanol (HPLC grade >99.9% purity) was obtained from the Mallinckrodt, Baker Inc. (Paris, Kentucky, USA) and ethanol (HPLC grade, >99.9% purity) was purchased from the J. T. Baker Inc.(Phillipsburg, New Jersey, USA). They are used directly without further purification. 2-Ethoxyethanol (HPLC grade, >99.9% purity) was obtained from the Junsei Chem. Co. Ltd. (Tokyo,

Japan) and 2-Methoxyethanol (HPLC grade, >99.9%) was from the Kanto Chem. Co. Inc. (Tokyo, Japan).

2-2. Apparatus and Procedure

The schematic diagram of the experimental apparatus that was newly designed and constructed in this work was shown in Fig. 1. The equipment consists of three major parts as the high-pressure equilibrium cell, pressure and temperature control parts, and sampling devices and analytic parts. The equilibrium cell in Fig. 1 was equipped with a sapphire glass window in order to view the inside of the cell. The cell volume is 50mL and it was designed to operate safely up to 25 MPa. Temperature was controlled within accuracy of $\pm0.1K$ by a PID controller (Hanyoung Electronic Co. Ltd., Seoul, Korea) with a forced-convection air-bath. Temperature was measured within the accuracy of $\pm0.05K$ by Pt-100• thermocouple. The equilibrium pressure was measured by a Heise gauge (Heise Co., Newtown, Connecticut, USA) within ±0.01 MPa. A hand pump (HIP Co., Erie, Pennsylvania, USA) was used to control pressure accurately. Using a circulation pump (Thermo Separation Products Inc., Riviera Beach, Florida, USA), the vapor and liquid phases were circulated until the system reaches to an equilibrium state.

CO_2 was fed by a gas booster (Hydro–Pac Inc., Pennsylvania, USA) and alcohol sample was fed by a liquid pump (Thermo Separation Products Inc., Riviera Beach, Florida, USA). The equilibrated samples of vapor and liquid phase were taken by a sampling valve (Rheodyne L.P., Rohnert Park, California, USA) and analyzed by an on-line gas chromatograph (GL science Inc., Tokyo, Japan). The internal volume of the sampling loop for vapor phase was 5μL and that of liquid phase was 1μL.

Experiments were carried out in the following manner. The entire internal loop of the apparatus including the equilibrium cell was rinsed several times by liquid CO_2 and the degree of cleanness was checked by analyzing the rinsed liquid CO_2 with the gas chromatograph. Then, the equilibrium cell was evacuated by a vacuum pump (Sinku Kiko Co. Ltd., Yokohama, Japan) and subsequently the CO_2 and alcohol sample were fed into the cell. By the circulation during 12 hours, the system reaches an equilibrium state. After that, samples were taken both vapor and liquid phase and analyzed. Sampling and analysis was repeated more than three times and the mean values were taken as the finally measured composition. Experiments were continued with increasing a pressure by charging CO_2 into the system. In the case of pressure near the critical point of a sample mixture, the circulation rate of each phase was significantly lowered to minimize the possible fluctuation of an equilibrium state and the equilibrium pressure was controlled with the hand pump.

3. Results and Discussion

3-1. Experimental Results

The vapor- and liquid-phase equilibrium data were taken for 4 different binary CO_2-alcohol systems at temperature ranges from 313.15 to 345.15K. The alcohol solutes chosen in the present study are methanol, ethanol, 2-methoxyethanol and 2-ethoxyethanol. At a fixed temperature, the vapor- and liquid-phase compositions were measured by varying the equilibrium pressure of the system. When the vapor- and liquid-phase compositions become identical, the pressure of the system was regarded as

a critical pressure of a sample binary CO_2-alcohol system. The experimental data taken for CO_2-alcohol systems in the present study were summarized in Tables 1 to 4. In these Tables, 'c' denotes the critical state of the system.

To conform the reliability of the apparatus, the VLE data of CO_2-methanol system was measured at 313.15K and they were compared together with the accurately reported literature data at 313.15 K by Ohgaki et al. [9]. This result was shown in Fig. 2. As one can see from Fig. 2, both the measure and existing data of CO_2-methanol system agree quantitatively well. In addition, similar measurement and comparison was made to CO_2-ethanol system at 313.4 K. In this comparison, the existing data was used the data reported by Suzuki et al. [10]. Upon scrutiny of those comparisons, we assume that the experimental apparatus devised in the present study is reliably enough for the data generation for basic design purposes.

3-2. MF-NLF-HB EOS

The MF-NLF-HB EOS is an extended version of the MF-NLF model formulated by the present authors previously [7,8] with the addition of the theory of hydrogen-bonding proposed by Veytzman [11]. Omitting derivational detail of the MF-NLF-HB model [12], the general expression of the model can be written as,

$$P = \frac{1}{\beta V_H}\left\{\frac{z}{2}\ln\left[1+\left(\frac{q_M}{r_M}-1\right)\rho\right]-\ln(1-\rho)-\upsilon_{HB}\rho++\frac{z}{2}\sum_{i=1}^{c}\theta_i\left(\frac{\tau_{0i}}{\sum_{k=0}^{c}\theta_k\tau_{ki}}-1\right)\right\} \quad (1)$$

where $q_M = \sum x_i q_i$, $r_M = \sum x_i r_i$, $\rho = \sum \rho_i$, $\rho_i = V_i^*/V$, $V_i^* = N_a r_i V_H$ and x_i is the mole fraction of species i in a mixture. The fraction of hydrogen bonds in the system,

υ_{HB} is given by the summed fraction of pairs of hydrogen bonds as follows

$$\upsilon_{HB} = \sum_{k=1}^{K}\sum_{l=1}^{L} N_{kl}^{HB} \Big/ \sum_{i=1}^{c} N_i r_i \qquad (2)$$

There are four molecular parameters in the MF-NLF-HB EOS for pure fluids; z, V_H, r_1 and ε_{11}. As in the previous study [13-16], we set $z = 10$ and $V_H = 9.75$ cm^{3}mol^{-1}. Thus, for a pure fluid we need to determine only two independent molecular parameters, r_1 and ε_{11}. The parameters r_1 and ε_{11} are regressed at each isotherm and represented as functions of temperature.

$$\varepsilon_{11} / k = E_a + E_b (T - T_0) + E_c \big[T\,ln(T_0 / T) + T - T_0 \big] \qquad (3)$$

$$r_1 = R_a + R_b (T - T_0) + R_c \big[T\,ln(T_0 / T) + T - T_0 \big] \qquad (4)$$

where $T_0 = 273.15$K is a reference temperature.

We have one binary energy parameter λ_{12} for a binary, which is defined by

$$\varepsilon_{12} = (\varepsilon_{11}\varepsilon_{22})^{1/2}(1 - \lambda_{12}) \qquad (5)$$

where λ_{12} is determined by data fitting and may be temperature dependent.

3-3. VLE Correlation

Measured VLE data for CO_2-alcohol systems were correlated with the Peng-Robinson and the MF-NLF-HB EOS. The basic property constants for the alcohols and

CO$_2$ were summarized in Table 5. Among alcohols, the critical constants and the acentric factor of 2-methoxyethanol and 2-ethoxyethanol were estimated by the Lydersen method [17]. Also, the energy and size parameters of the pure alcohols and CO$_2$ for the MF-NLF-HB model were estimated by using the liquid density data reported elsewhere [17,18]. Estimated values of the coefficients for Eqs. 3 and 4 are summarized in Table 6 for pure chemicals.

For each CO$_2$-alcohol system, the regressed binary adjustable interaction energy parameters, λ_{12} and the AAD for MF-NLF-HB model and Peng-Robin EOS were summarized in Table 7. In Table 7, calculated λ_{12} of EOS model are the independent constants with respect to the variation of the whole range of temperatures. As one can see from Table 7, the AAD of the MF-NLF-HB was slightly lower than the case of the Peng-Robinson model. Especially, the AADx of MF-NLF-HB model for CO$_2$-2-methoxyethanol and CO$_2$-2-ethoxyethanol was much lower than the case of Peng-Robinson model.

The experimental data and correlated results for the four CO$_2$-alcohol systems were shown in Figs. 3 ~ 6. In Figs. 3 and 4, the correlated results by the Peng-Robinson model with the temperature-independent λ_{12} show better fitting results than the case of the MF-NLF-HB model in general. The Peng-Robinson model was superior to the MF-NLF-HB model in the critical region. However, the inaccurate correlation capability of the MF-NLF-HB model for data in the critical region and the data of low-molecular weight species such as methanol or ethanol was not unexpected. The MF-NLF-HB model was based on the mean-field approximation of the r-mer lattice statistical-mechanical theory and it has such limitation in the critical region. Besides, upon the experiences of the present authors, the MF-NLF-HB model fits very accurately the VLE

data of high-molecular weight systems than any other models in the same genre. Except for the immediate critical region and for the very low molecular weight C_1, the utility of the MF-NLF-HB model was extensively proven elsewhere [8,12].

Measured data and calculated results for CO_2-2-methoxyethanol and CO_2-2-ethoxyethanol systems by the two models were shown in Figs. 5 and 6. For these illustrative high molecular weight systems containing alcohol, the results by the MF-NLF-HB was comparable to the Peng-Robinson EOS. The MF-NLF-HB model again showed some fitting inaccuracy when the equilibrium temperature and pressure reach to the immediate critical region of the systems.

4. Conclusion

By constructing a new circulation type high-pressure view cell, VLE of four industrially important systems containing CO_2 and alcohol were measured quantitatively. Also, the apparatus could be used to produce VLE data in the immediate critical region.

The measured data could be correlated quantitatively by the Peng-Robinson EOS and the MF-NLF-HB EOS which was specifically taken into account the existence of interaction due to the hydrogen bonding. The MF-NLF-HB model could correlate accurately the liquid phase composition. However, the MF-NLF-HB model experienced some inaccuracy in the calculation of VLE in the critical region. In general, the Peng-Robinson model fit the data better than the model proposed by the present authors for systems with low molecular weight alcohol.

5. List of symbols

N_a Avogadro's number

N_i number of molecular species i

P   pressure(MPa)

q_i surface area parameter

q_M mole fraction average of q_i

r_i segment number

r_M mole fraction average of r_i

T   temperature(K)

V   molar volume($cm^3 mol^{-1}$)

V^* characteristic volume of component i($cm^3 mol^{-1}$)

V_H volume of a unit cell (cm^3)

z   lattice coordination number

Greek letters

ε_{ij} interaction energy for *i-j* segment contacts(J)

λ_{ij} binary interaction parameter for *i-j* contacts

ρ total segment fraction

ρ_i segment fraction of component i

θ_i surface area fraction of component *I*

τ_{ij} nonrandomness factor

Superscripts

HB   chemical contribution by HB

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Tables

Table 1. Measured vapor-liquid equilibrium data for $CO_2(1)$-methanol(2) system

P (MPa)	x_1	y_1	P (MPa)	x_1	y_1	P (MPa)	x_1	y_1
T=313.15 K								
0.69	0.0424	0.0977	6.57	0.4555	0.9846	8.06	0.9147	0.9688
1.71	0.0977	0.9702	7.51	0.6154	0.9811	8.07	0.9277	0.9652
2.73	0.1479	0.9781	7.84	0.7651	0.9757	8.10	0.9298	0.9635
3.78	0.2199	0.9832	7.93	0.8218	0.9743	8.12	0.9350	0.9452
4.88	0.2972	0.9859	7.97	0.8597	0.9728	8.15(c)	0.9351	
5.60	0.3546	0.9857	7.99	0.8968	0.9745			
T=320.15 K								
0.60	0.0326	0.9150	6.50	0.3750	0.9804	8.88	0.8287	0.9441
1.63	0.0838	0.9582	7.29	0.4473	0.9787	8.92	0.8719	0.9297
2.69	0.1371	0.9717	8.14	0.5505	0.9738	8.93	0.8791	0.9010
3.70	0.1913	0.9778	8.62	0.6757	0.9662	8.95(c)	0.8860	
4.72	0.2505	0.9795	8.82	0.7750	0.9555			
5.72	0.3166	0.9815	8.85	0.8053	0.9484			
T=330.00 K								
0.78	0.0346	0.8857	6.07	0.2845	0.9725	10.48	0.7401	0.8777
1.26	0.0550	0.9257	7.32	0.3616	0.9709	10.51	0.7601	0.8684
2.24	0.0960	0.9537	8.90	0.4836	0.9647	10.55	0.7694	0.8619
3.12	0.1342	0.9610	9.42	0.5382	0.9584	10.57	0.8215	0.8572
4.04	0.1757	0.9667	9.85	0.5998	0.9489	10.59(c)	0.8243	
5.17	0.2365	0.9717	10.22	0.6779	0.9438			
T=335.65 K								
0.84	0.0336	0.8592	7.44	0.3247	0.9664	11.25	0.6762	0.8901
1.69	0.0666	0.9217	8.57	0.3924	0.9641	11.35	0.6933	0.8698
3.08	0.1208	0.9502	9.32	0.4471	0.9583	11.42	0.7113	0.8691
4.41	0.1768	0.9620	10.28	0.5330	0.9466	11.44	0.7759	0.8250
5.52	0.2262	0.9659	10.82	0.6003	0.9295	11.45	0.7925	0.8059
6.52	0.2760	0.9671	11.15	0.6651	0.8948	11.46(c)	0.7940	
T=342.80 K								
0.67	0.0247	0.7999	8.40	0.3427	0.9574	12.21	0.6719	0.8526
2.00	0.0728	0.9148	9.41	0.3993	0.9523	12.35	0.7210	0.8072
3.13	0.1145	0.9403	10.41	0.4664	0.9432	12.37	0.7311	0.8026
4.20	0.1553	0.9510	11.10	0.5234	0.9312	12.39	0.7603	0.7720
5.23	0.1961	0.9559	11.64	0.5806	0.9108	12.40(c)	0.7610	
6.32	0.2425	0.9588	11.89	0.6138	0.8943			
7.37	0.2909	0.9586	12.23	0.6792	0.8498			

Table 2. Measured vapor-liquid equilibrium data for CO_2(1)-ethanol(2) system

P (MPa)	x_1	y_1	P (MPa)	x_1	y_1	P (MPa)	x_1	y_1
T=313.40 K								
0.57	0.0337	0.9614	5.44	0.3401	0.9899	8.04	0.9451	0.9738
1.45	0.0821	0.9807	6.44	0.4506	0.9885	8.11	0.9668	0.9672
2.59	0.1456	0.9880	7.34	0.6253	0.9849	8.16(c)	0.9630	
3.38	0.1937	0.9892	7.66	0.7619	0.9824			
4.35	0.2564	0.9903	7.94	0.9293	0.9799			
T=322.50 K								
0.57	0.0302	0.9406	5.86	0.3180	0.9855	8.98	0.7878	0.9645
1.56	0.0781	0.9724	6.85	0.3975	0.9841	9.08	0.8504	0.9571
2.56	0.1272	0.9804	7.74	0.4887	0.9809	9.14	0.9162	0.9470
3.81	0.1908	0.9844	8.46	0.6091	0.9753	9.18	0.9192	0.9297
4.85	0.2514	0.9853	8.79	0.7056	0.9704	9.21(c)	0.9198	
T=333.40 K								
0.66	0.0285	0.9141	7.18	0.3456	0.9780	10.45	0.7333	0.9299
1.65	0.0697	0.9607	7.90	0.3955	0.9752	10.59	0.7539	0.9202
2.73	0.1172	0.9716	8.70	0.4629	0.9707	10.61	0.8323	0.8906
3.75	0.1618	0.9750	9.54	0.5534	0.9647	10.64(c)	0.8633	
4.75	0.2102	0.9788	10.03	0.6300	0.9556			
5.83	0.2666	0.9778	10.37	0.7091	0.9373			
T=338.80 K								
0.61	0.0269	0.8866	7.92	0.3685	0.9718	11.17	0.7554	0.8938
1.59	0.0659	0.9472	8.97	0.4415	0.9664	11.24	0.7756	0.8861
2.68	0.1097	0.9630	9.79	0.5154	0.9598	11.28	0.8596	0.8713
3.68	0.1513	0.9692	10.39	0.5869	0.9507	11.31(c)	0.8601	
4.79	0.2005	0.9723	10.87	0.6691	0.9295			
5.86	0.2518	0.9734	11.12	0.7310	0.9046			
6.92	0.3087	0.9733	11.16	0.7364	0.9030			
T=344.75 K								
0.80	0.0307	0.8727	7.06	0.2941	0.9679	11.63	0.6720	0.9076
1.81	0.0692	0.9323	8.16	0.3535	0.9654	11.84	0.7149	0.8863
2.83	0.1082	0.9543	9.28	0.4253	0.9614	11.86	0.7449	0.8667
3.88	0.1492	0.9617	10.27	0.5024	0.9523	11.90	0.7734	0.8494
4.94	0.1944	0.9664	10.99	0.5785	0.9408	11.93	0.8008	0.8068
6.03	0.2448	0.9678	11.40	0.6346	0.9252	11.97(c)	0.8020	

Table 3. Measured vapor-liquid equilibrium data for CO_2(1)-2-methoxyethanol(2) system

P (MPa)	x_1	y_1	P (MPa)	x_1	y_1	P (MPa)	x_1	y_1
T=322.90 K								
1.41	0.0860	0.9999	5.28	0.3348	0.9957	9.27	0.9002	0.9764
2.20	0.1316	0.9999	6.72	0.4579	0.9945	9.34	0.9383	0.9730
3.26	0.1961	0.9959	7.35	0.5222	0.9933	9.40	0.9535	0.9638
4.34	0.2675	0.9959	8.44	0.6834	0.9896	9.41(c)	0.9616	
T=329.80 K								
1.32	0.0730	0.9999	6.96	0.4197	0.9926	10.32	0.8877	0.9435
2.36	0.1255	0.9918	7.73	0.4834	0.9912	10.36	0.9141	0.9359
3.37	0.1795	0.9938	8.45	0.5518	0.9893	10.39(c)	0.9147	
4.38	0.2396	0.9937	9.36	0.6606	0.9845			
5.46	0.3055	0.9936	10.13	0.8233	0.9719			
T=336.65 K								
1.32	0.0673	0.9862	7.91	0.4368	0.9904	11.30	0.8585	0.9459
2.46	0.1211	0.9911	9.11	0.5327	0.9863	11.33	0.8753	0.9360
3.40	0.1669	0.9923	9.89	0.6081	0.9831	11.35	0.9143	0.9316
4.61	0.2319	0.9928	10.66	0.7168	0.9743	11.38	0.9156	0.9266
5.76	0.2965	0.9927	11.23	0.8244	0.9559	11.41(c)	0.9167	
6.83	0.3626	0.9919	11.26	0.8414	0.9491			
T=343.70 K								
1.19	0.0576	0.9997	8.30	0.4543	0.9865	12.31	0.8144	0.9341
2.61	0.1183	0.9870	10.02	0.5365	0.9826	12.37	0.8371	0.9229
4.10	0.1878	0.9906	11.01	0.6222	0.9757	12.40	0.8976	0.9105
5.78	0.2715	0.9905	11.50	0.6727	0.9694	12.46(c)	0.9086	
6.85	0.3298	0.9903	11.96	0.7432	0.9550			
7.88	0.3890	0.9884	12.17	0.7845	0.9471			

Table 4. Measured vapor-liquid equilibrium data for CO_2(1)-2-ethoxyethanol(2) system

P (MPa)	x_1	y_1	P (MPa)	x_1	y_1	P (MPa)	x_1	y_1
T=323.30 K								
1.29	0.0885	0.9997	7.35	0.5587	0.9999	9.34	0.9690	0.9750
2.76	0.1802	0.9998	8.95	0.8134	0.9999	9.35(c)	0.9749	
4.35	0.2889	0.9999	9.29	0.9289	0.9815			
5.88	0.4134	0.9999	9.31	0.9451	0.9778			
T=330.00 K								
1.58	0.0980	0.9997	7.63	0.5130	0.9999	10.15	0.8838	0.9741
2.97	0.1781	0.9998	8.68	0.6170	0.9999	10.26	0.9241	0.9611
4.57	0.2834	0.9999	9.64	0.7673	0.9868	10.31	0.9361	0.9531
6.44	0.4077	0.9999	10.03	0.8530	0.9793	10.35(c)	0.9445	
T=337.15 K								
1.36	0.0788	0.9995	7.38	0.4368	0.9999	11.09	0.8412	0.9665
2.86	0.1580	0.9999	9.03	0.5695	0.9899	11.24	0.8759	0.9551
4.48	0.2477	0.9999	10.26	0.7019	0.9853	11.28	0.9043	0.9459
6.00	0.3417	0.9999	10.80	0.7798	0.9775	11.35(c)	0.9225	
T=344.10 K								
1.96	0.1026	0.9996	8.02	0.4381	0.9914	12.19	0.9342	0.9499
3.46	0.1753	0.9999	9.43	0.5321	0.9883	12.31	0.8723	0.9331
4.86	0.2489	0.9999	10.67	0.6379	0.9814	12.37	0.8944	0.9052
6.52	0.3411	0.9928	11.59	0.7365	0.9750	12.44(c)	0.9044	

Table 5. Physical properties of chemicals used in this work

Chemicals	MW	Tb (K)	Tc (K)	Pc (MPa)	W
CO_2	44.01	216.6	304.1	7.38	0.239
Methanol	32.04	337.7	512.6	8.09	0.556
Ethanol	46.07	351.4	513.9	6.14	0.644
2-Methoxyethanol	76.10	397.5	564.0	5.01	0.733
2-Ethoxyethanol	90.12	408.2	569.0	4.24	0.758

Table 6. Coefficients of molecular parameters for eqs.(3) and (4)

Chemicals	Ea	Eb	Ec	Ra	Rb	Rc
CO_2	85.91302	-0.10298	-0.36562	3.51652	0.00146	-0.00134
Methanol	109.3322	0.05421	0.20347	35.7308	-0.00422	-0.06748
Ethanol	105.1603	-0.00365	-0.02383	50.6421	-0.02175	-0.07891
2-Methoxyethanol	86.8943	0.46966	1.08885	49.66829	0.30806	0.68697
2-Ethoxyethanol	82.2498	0.50184	1.18591	61.95841	0.40497	0.98520

The values of coefficients are reliable in the temperature range of 253-513K

Table 7. Binary interaction parameter for and average absolute deviation for the equilibrium data

System	Model	λ_{12}	AADx(%)	AADy(%)
CO_2 + methanol	PR EOS	0.0734	7.48	5.28
	MF-NLF-HB EOS	0.0036	4.90	2.74
CO_2 +ethanol	PR EOS	0.0908	9.98	4.12
	MF-NLF-HB EOS	0.0485	8.18	3.13
CO_2 + 2-methoxyethanol	PR EOS	0.0475	15.7	2.78
	MF-NLF-HB EOS	0.0412	7.50	1.89
CO_2 + 2-ethoxyethanol	PR EOS	0.0013	26.2	4.28
	MF-NLF-HB EOS	0.0496	8.17	1.07

$$AADx(\%) = \frac{1}{N} \sum_J \left| (x_j^{cal} - x_j^{exp})/x_j^{exp} \right| \times 100$$

$$AADy(\%) = \frac{1}{N} \sum_J \left| (y_j^{cal} - y_j^{exp})/y_j^{exp} \right| \times 100$$

Figure Captions

Fig. 1. Schematic diagram of experimental apparatus: (1)Gas Chromatograph; (2)Sampling valve; (3)Equilibrium cell; (4)Circulation pump; (5)Air bath; (6)Pressure gauge; (7)Hand pump; (8)Pressure transducer; (9)Reservoir; (10) Gas charging pump; (11)CO2 gas cylinder; (12)Vaccum pump (13) Liquid charging pump.

Fig. 2. Comparison of measured and reported vapor-liquid equilibrium data for CO_2-methanol system at 313.15 K.

Fig. 3. Comparison of measured data with correlated values by MF-NLF-HB EOS and P-R EOS for CO_2-methanol system.

Fig. 4. Comparison of measured data with correlated values by MF-NLF-HB EOS and P-R EOS for CO_2-ethanol system.

Fig. 5. Comparison of measured data with correlated values by MF-NLF-HB EOS and P-R EOS for CO_2-2-methoxyethanol system.

Fig. 6. Comparison of measured data with correlated values by MF-NLF-HB EOS and P-R EOS for CO_2-2-ethoxyethanol system.
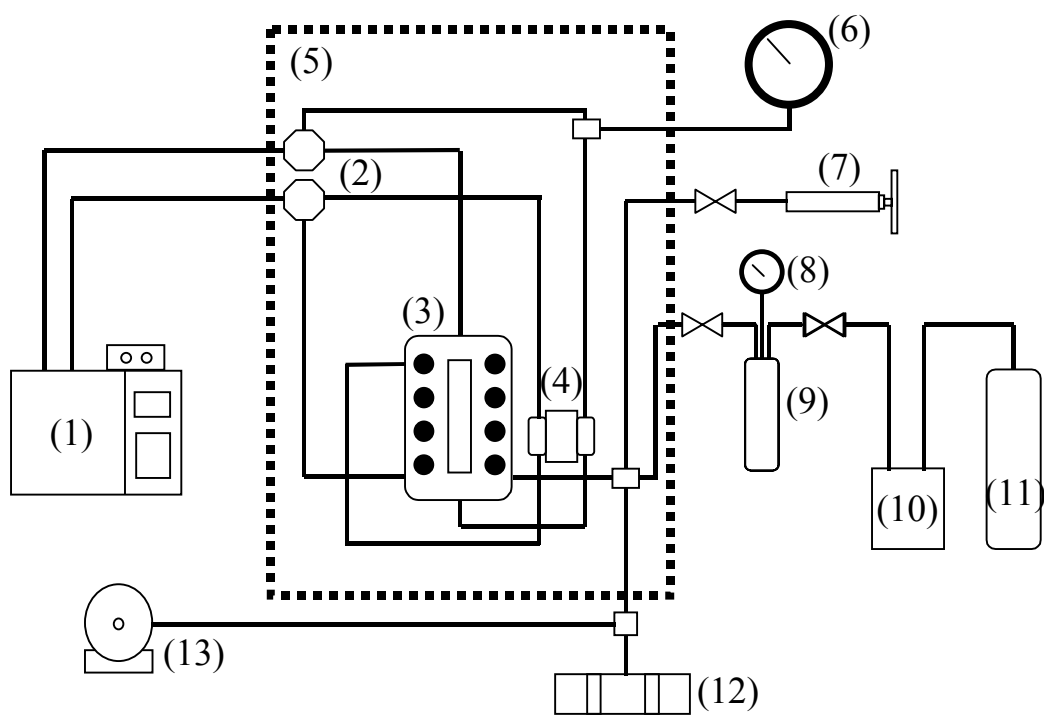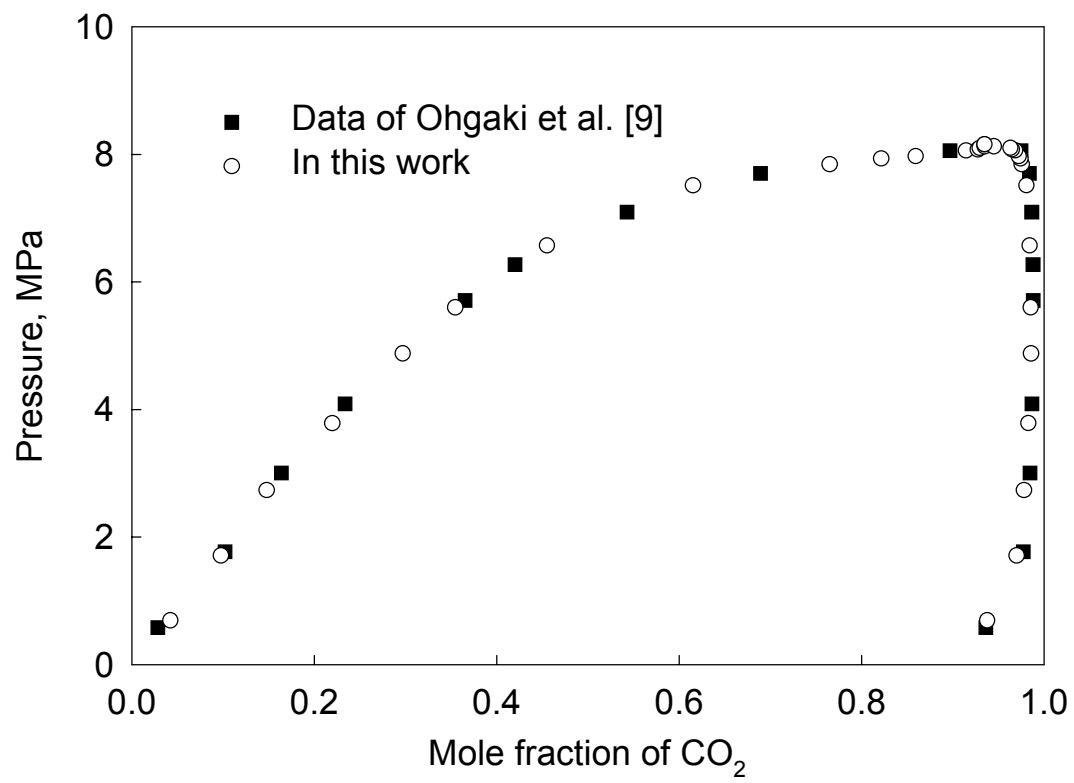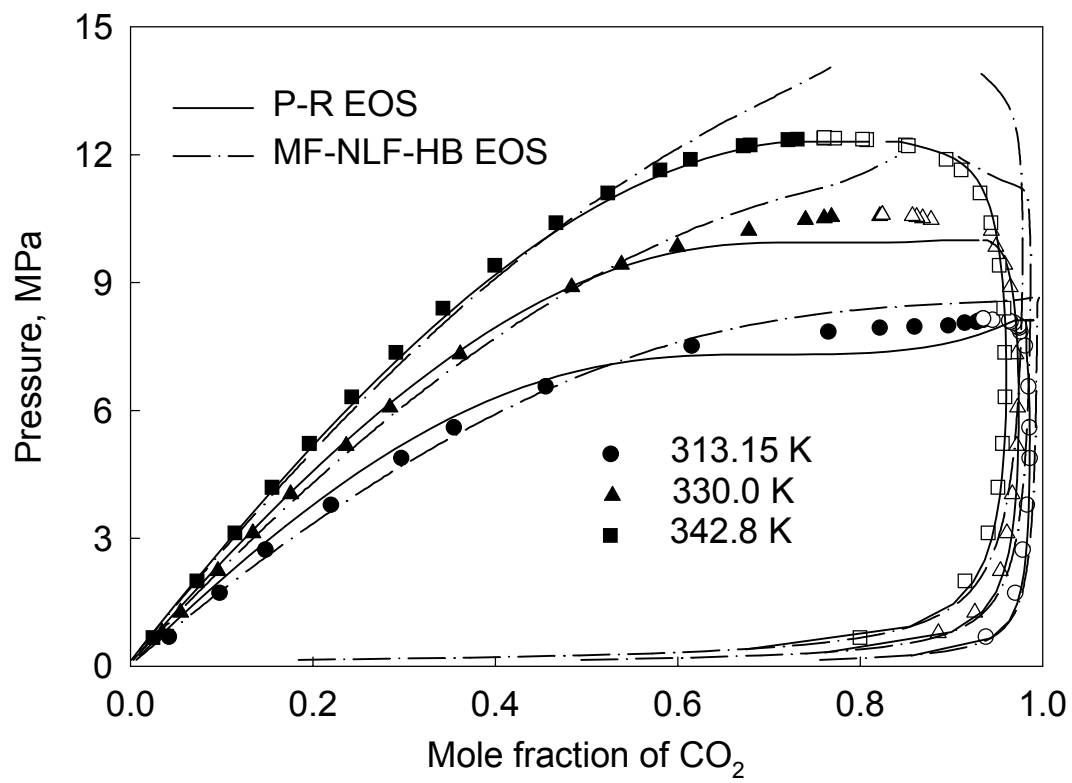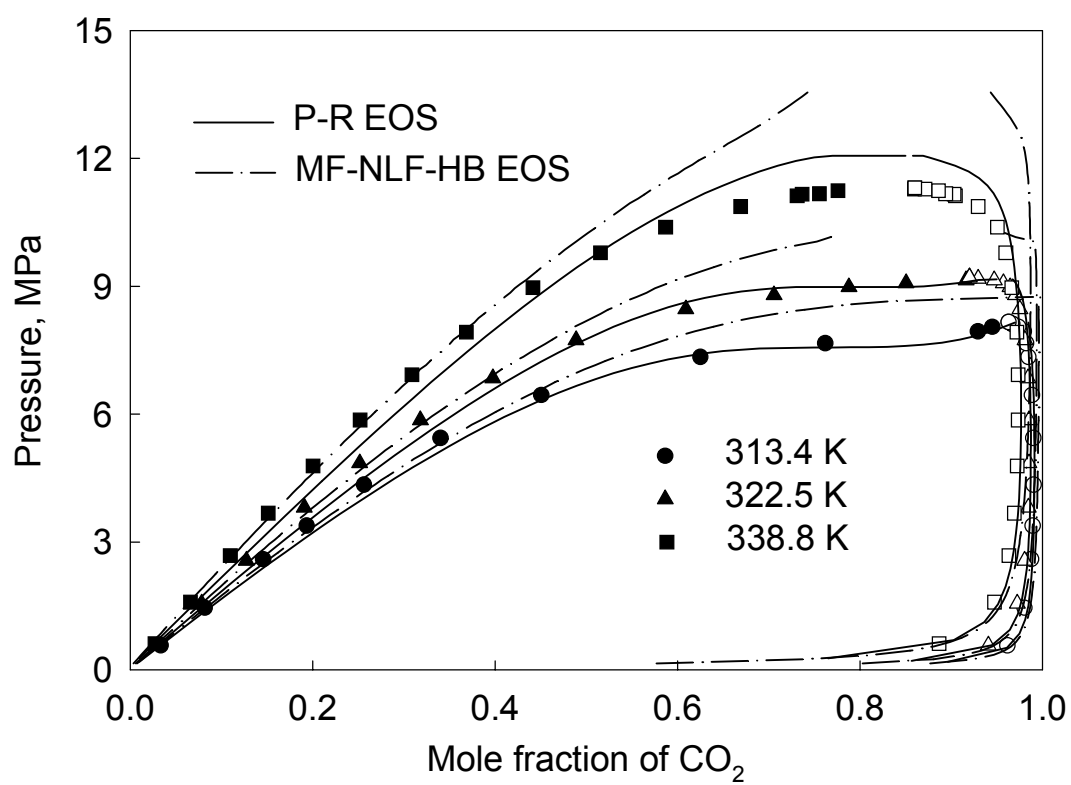
Fig. 1.

Fig. 2.

Fig. 3.

Fig. 4.

Fig. 5.

Fig. 6.